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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
G01J 3/06, G02B 26/08, G01J 3/30

A1

(11) International Publication Number: WO 96/34256

(43) International Publication Date: 31 October 1996 (31.10.96)

(21) International Application Number: PCT/GB96/00970

(22) International Filing Date: 24 April 1996 (24.04.96)

(30) Priority Data:
9508343.2 25 April 1995 (25.04.95) GB

(71) Applicant (*for all designated States except US*): RENISHAW PLC [GB/GB]; New Mills, Wotton-under-Edge, Gloucestershire GL12 8JR (GB).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): BATCHELDER, David, Neville [GB/GB]; 2A Foxhill Avenue, Leeds, Yorkshire LS16 5PB (GB).

(74) Agent: JACKSON, John, Timothy; Renishaw plc, Patent Dept., New Mills, Wotton-under-Edge, Gloucestershire GL12 8JR (GB).

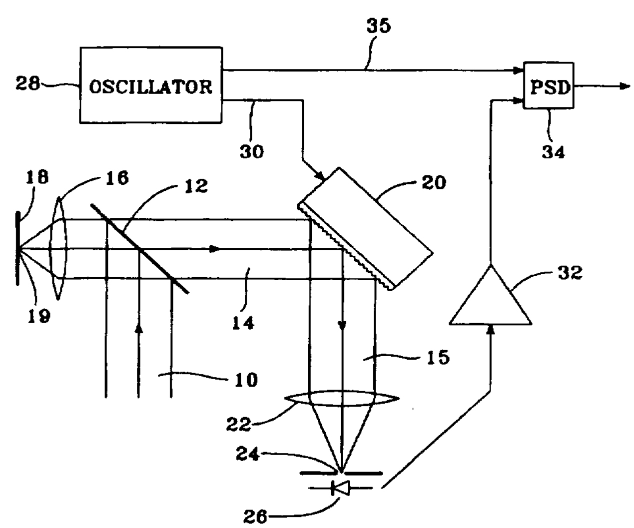
(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

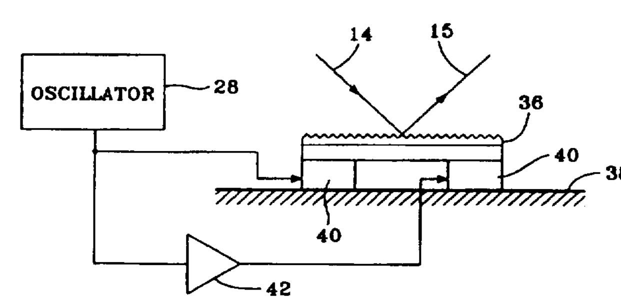
Published
With international search report.

(54) Title: SPECTROSCOPIC APPARATUS

(57) Abstract

A line in a Raman spectrum scattered from a sample (18) is selected by a diffraction grating (20) and passed to a detector (26). The grating (20) may be based on an electrostrictive device and has a variable pitch. It is tuned about the selected Raman line under the control of an oscillator (28). The output from the detector (26) is analysed synchronously with the oscillation by a phase sensitive detector (34). This rejects background light and enables, for example, confirmation of the existence of the Raman line in the spectrum, and measurement of its height above the background. The variable pitch grating (20) may be replaced by a fixed pitch grating or a tunable filter, mounted on an oscillatory drive which may comprise electrostrictive or piezolelectric elements.





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SPECTROSCOPIC APPARATUS

This invention relates to spectroscopy.

Spectroscopic apparatus for analysing the Raman spectrum of a sample is disclosed in, for example, our European Patent Application No. EP 543578. A sample is illuminated by monochromatic laser light, and the resulting Raman scattered light is analysed, either by a diffraction grating which disperses the Raman spectrum, or by a non-dispersive tunable filter (e.g. an interference filter).

In one aspect, the present invention relates to spectroscopic apparatus having a diffraction grating for dispersing a spectrum, the diffraction grating having a variable pitch. In other aspects of the invention, the variable pitch diffraction grating may be replaced by a diffraction grating or filter which is tunable, for example by rotating it about an axis perpendicular to the optical axis.

Preferred embodiments of the invention will now be described by way of example, with reference to the accompanying drawings, wherein:

Fig 1 is a schematic diagram of a first Raman spectrometer, and

Fig 2 is a schematic diagram of part of a modified Raman spectrometer.

In Fig 1, an incoming laser beam 10 is reflected through 90° by a dichroic filter 12 placed at 45° to the optical path. It is focused by a lens 16 to a spot 19 on a sample 18. Raman scattered light produced from the sample 18 as a result is collected by the lens 16 and passes back through the system. The Raman scattered light 14 is transmitted by the dichroic filter 12, while Rayleigh scattered light at

the same frequency as the incoming laser beam is rejected by this filter. The Raman scattered light 14 is incident upon a diffraction grating 20, which reflects a dispersed spectrum of the Raman light. Light 15 of one particular Raman peak of interest within this spectrum is focused by a lens 22 onto a slit 24, which may for example accept only $20cm^{-1}$ of the dispersed spectrum. This slit 24 thus acts to select a particular Raman line of interest in the spectrum produced by the sample 18. The light passing through the slit 24 is detected by a suitable detector, such as an avalanche photodiode 26. Of course, the slit 24 may accept a narrower or wider band than $20cm^{-1}$, if desired.

Any desired Raman line of interest may be selected by rotating the diffraction grating 20 about an axis normal to the optical axis, so that the desired Raman line is focused on the slit 24.

The diffraction grating 20 has a variable pitch. It may be based upon an electrostrictive device, the grating pitch varying in accordance with a variable voltage applied to the electrostrictive device. In one example of such a device, the grating may be recorded holographically, e.g. in a gelatin film which is provided on an electrostrictive substrate. A suitable variable diffraction grating based upon an electrostrictive device has recently been proposed by Cookson Technology Centre, Sandy Lane, Yarnton, Kidlington, Oxfordshire, OX5 1PF, United Kingdom.

In the arrangement shown in Fig 1, the electrostrictive device in the grating 20 is driven from an oscillator 28, producing (for example) a sinusoidal output on a line 30. In response to this, the pitch of the grating 20 varies sinusoidally with time, e.g. by about 0.2%. This produces a corresponding variation in the wavenumber of the Raman light selected by the slit 24. Typically, the variation is sufficient to enable scanning between the point of maximum intensity on a desired Raman peak and a point just off the

peak where only background light is received, e.g. caused by thermal effects, fluorescence, etc.

For best results, the output 30 of the oscillator 28 should consist of the desired oscillation, superimposed on a DC level. Otherwise, if the electrostrictive device is operated by a signal which alternates about zero, it will cause frequency doubling and harmonic distortion.

The output signal from the detector 26 is taken via signal conditioning circuitry 32 to a phase sensitive detector (PSD) 34. The PSD 34 also receives an output 35 from the oscillator 28, which is synchronous with the AC component on the output 30. The PSD 34 therefore produces an output representing the scanned Raman peak, from which its intensity (height) may easily be determined. Noise and the DC component produced by the thermal background, fluorescence etc. are rejected by the PSD 34.

The apparatus described has a number of possible uses. It can be used in various process control applications. For example, it may be used to monitor the growth of a diamond film by chemical vapour deposition, the grating 20 and slit 24 being arranged to scan the characteristic Raman peak of diamond at $1332cm^{-1}$. The apparatus is also useful in situations in which one is looking to see if a given Raman line appears, e.g. during chromatography. The technique described gives a null signal until the Raman line appears.

The apparatus described has the advantage that there are no mechanical moving parts.

Although it has been described in relation to Raman spectroscopy, the described apparatus and techniques can be used to examine the lines produced in any other kind of spectroscopy. Furthermore, the apparatus can have various extra components or modifications, e.g. as suggested in our European application no. EP 543578. It is also possible to

provide separate laser illumination of the sample 18, rather than injecting the laser beam 10 via the filter 12.

Fig 2 shows a modified apparatus. Most of the apparatus is the same as Fig 1, and has therefore not been shown in Fig 2. However, in place of the variable pitch diffraction grating 20, a fixed pitch diffraction grating 36 is used. This is mounted onto a mounting plate 38 via an oscillatory drive comprising two electrostrictive devices 40. One of these electrostrictive devices 40 is driven directly from the oscillator 28, while the other is driven in anti-phase via an inverter 42. The result is to produce a rocking motion of the diffraction grating 36 relative to the mounting plate 38. The result is the same as in the apparatus of Fig 1: the part of the spectrum which is selected by the slit 24 can be made to scan a Raman line of interest at the frequency of the oscillator 28. Piezoelectric devices may be used in place of the electrostrictive devices 40, if desired. Other oscillatory drives can also be used, for example the grating 36 may be mounted on a rotary table which can be oscillated by a suitable motor.

In a further modification (not shown) a tunable narrow band filter (e.g. an interference filter) may be used in place of the diffraction grating 20 or 36. Such a filter is tuned by rotating it to a desired tilt angle about an axis which is normal to the optical axis. In the present case, a suitable rotary drive is used to oscillate the filter about this tilt axis, at the frequency of the oscillator 28.

CLAIMS:

1. Spectroscopic apparatus in which a spectrum of light is received from a sample and analysed, comprising:

a detector;

means for selecting a line from said spectrum and passing it to the detector, said selecting means being tunable at least about said line in response to an input signal;

an oscillator connected to the selecting means to provide said input signal, whereby the selecting means oscillates about said line and passes the resulting light to the detector; and

a signal processing circuit connected to the detector to analyse said line.

2. Spectroscopic apparatus according to claim 1, in which the signal processing circuit comprises a phase sensitive detector which is also connected to the oscillator, whereby said line is analysed synchronously with the oscillation of the selecting means about said line.

3. Spectroscopic apparatus according to claim 1 or claim 2, wherein the selecting means comprises a diffraction grating having a pitch which is variable in response to said input signal.

4. Spectroscopic apparatus according to claim 3, wherein the diffraction grating comprises an electrostrictive device.

5. Spectroscopic apparatus according to claim 1 or claim 2, wherein the selecting means comprises a diffraction grating, mounted on an oscillatory drive driven by the oscillator.

6. Spectroscopic apparatus according to claim 1 or claim 2, wherein the selecting means comprises a tunable filter, mounted on an oscillatory drive driven by the oscillator.

7. Spectroscopic apparatus according to claim 5 or claim 6, wherein the oscillatory drive comprises at least one electrostrictive or piezoelectric device for rocking the selecting means.

8. Spectroscopic apparatus in which a spectrum of light is received from a sample and analysed, comprising:

a detector; and

a diffraction grating for dispersing the spectrum and passing at least a line from said spectrum to the detector, said diffraction grating having a pitch which is variable in response to an input signal.

9. Spectroscopic apparatus according to claim 8, wherein the diffraction grating comprises an electrostrictive device.

Fig.1

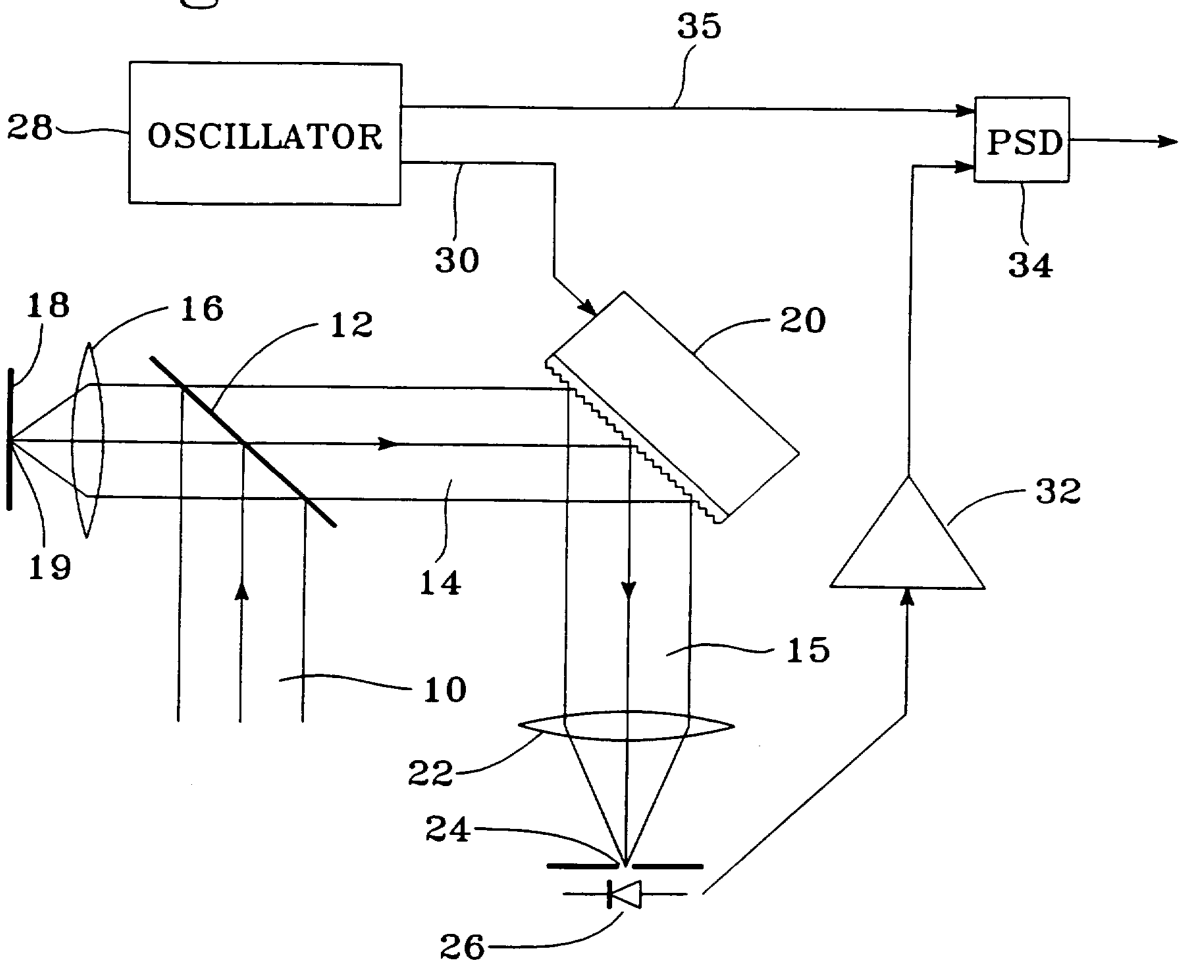
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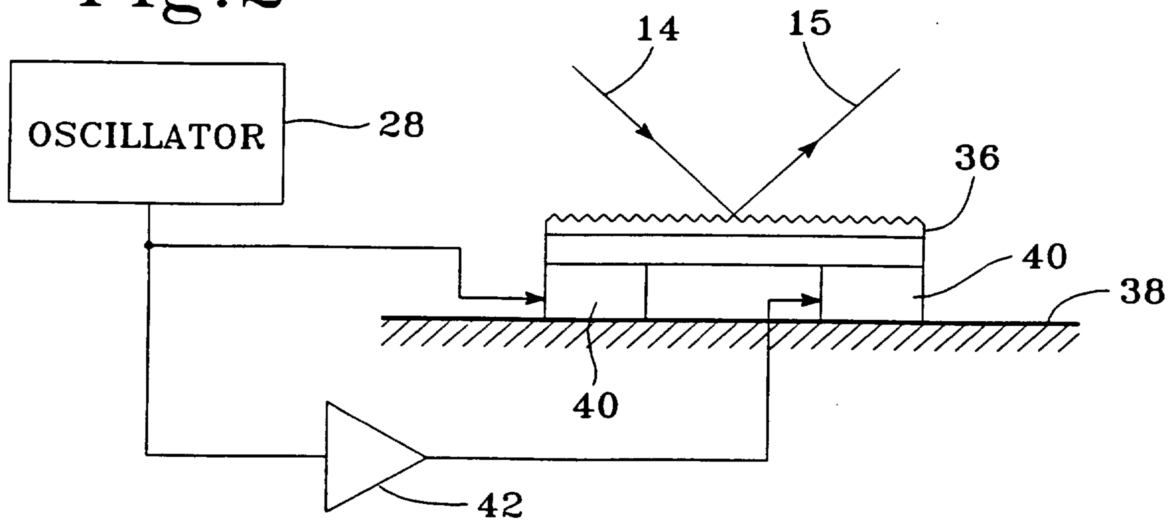
Fig.2


OSCILLATOR
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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/00970

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01J3/06 G02B26/08 G01J3/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G01J G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE,A,39 43 387 (AKAD WISSENSCHAFTEN DDR) 5 July 1990	1-4,7-9
Y	see the whole document	5,6
Y	US,A,5 225 888 (SELWYN GARY S ET AL) 6 July 1993 see column 10; figures 5,6	6
Y	EP,A,0 510 856 (SIEMENS PLESSEY CONTROLS LTD) 28 October 1992 see the whole document	6
Y	US,A,4 835 393 (KRAUSS LUTZ) 30 May 1989 see column 6, last paragraph see column 7, line 30 - line 44; figure 1	5

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[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
30 July 1996	09.08.96

Name and mailing address of the ISA	Authorized officer
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	WOLFGANG DEMTRÖDER: "Laserspektroskopie, Grundlagen und Techniken" 1993 , SPRINGER , BERLIN XP002009680 see page 293 - page 294, paragraph 1 -----	2

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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